Electroisomerization

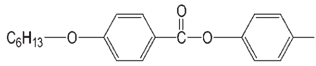
DOI: 10.1002/anie.200705699

Fast *Cis–Trans* Isomerization of an Azobenzene Derivative in Liquids and Liquid Crystals under a Low Electric Field[**]

*Xia Tong, Maxime Pelletier, Andrzej Lasia, and Yue Zhao**

Reversible *trans–cis* photoisomerization of azobenzene and its derivatives has been extensively studied and exploited as a photoswitch in numerous molecular systems and functional materials.[1] Thermally activated *cis–trans* isomerization is also well understood, the rate of which depends on the substituents on the azobenzene and the environment surrounding the chromophore.[1,2] Little attention has been paid to the effect of an electric field on the isomerization of azobenzene. Fujishima et al. first reported an electrochemical process inducing the conversion of *cis*-azobenzene to *trans*-azobenzene.[3] With amphiphilic azobenzene derivatives forming a Langmuir–Blodgett (LB) monolayer film on an electrode, *cis*-azobenzene formed on UV irradiation can be reduced to hydrazobenzene (two-electron reduction in aqueous solution), which is then reoxidized to *trans*-azobenzene. This coupled photochemical and electrochemical isomerization was suggested for high-density information storage.[3] Later, the same group found that *cis*-azobenzene in such an LB monolayer could return to the *trans* isomer by an electrostatic process involving no redox reaction.[4] Since the azobenzene derivative was deposited on the working electrode dipped in an electrolyte solution, *cis–trans* isomerization was attributed to the interaction of azobenzene with the high electric field on the order of $10^3\,\mathrm{V\,\mu m^{-1}}$ present in the electrical double layer. However, the underlying mechanism remains unknown, since even with a high field of $10^3\,\mathrm{V\,\mu m^{-1}}$, direct interaction with azobenzene, the *trans* and *cis* isomers of which have different dipole moments ($\Delta\mu \approx 3$ D for unsubstituted azobenzene) cannot be responsible for a drastic lowering of the *cis–trans* isomerization barrier.[4] More recently, reversible *cis–trans* isomerization of individual azobenzene molecules on a metal surface was achieved by scanning tunneling microscopy (STM), first with tunneling electrons[5] and then by means of the electric field at the STM junction.[6] In the latter case, the measured threshold voltage for *cis–trans* isomerization was also in the range of $10^3\,\mathrm{V\,\mu m^{-1}}$. The effect of high electric fields on the isomerization of other chromophores was also reported.[7] Here we report the astonishing finding that with an azobenzene derivative dissolved in liquids or liquid crystals, a low static electric field applied on the mixture between two conductive electrodes can induce fast *cis–trans* isomerization. In benzonitrile, for instance, the rate constant of *cis–trans* isomerization under an external field strength of $1\,\mathrm{V\,\mu m^{-1}}$ could be six orders of magnitude faster than thermal isomerization in the absence of the field. We show that this drastic electric-field-induced effect could have important implications for doped liquid crystals using azobenzene as a photoswitch to control the electrooptical properties.

The *cis–trans* isomerization of the used azobenzene derivative, 4-hexyloxy-4′-(4-hexyloxybenzoate)azobenzene (HHBAzo),[8] proceeded very slow in solution at ca. 22 °C in the dark. Figure 1 a shows the UV/Vis spectra of a solution of HHBAzo in benzonitrile (ca. 3 wt %), which was filled into a parallely rubbed indium-tin-oxide (ITO)-coated liquid-crystal (LC) cell with a 5-μm gap (E.H.C. Japan). As the cell is transparent to $\lambda > 330$ nm, the absorption peak of the *trans*-azobenzene at about 360 nm (π–π* transition) can clearly be seen. After UV irradiation of the solution (ca. 365 nm, $15\,\mathrm{mW\,cm^{-2}}$, 10 s), disappearance of this peak indicates efficient *trans–cis* photoisomerization. The weak absorption peak of the *cis*-azobenzene around 450 nm (n–π* transition) is difficult to see due to the undulating baseline caused by the interference of the glass cell. The spectrum recorded one hour after UV irradiation is almost unchanged owing to the very slow thermal conversion of the *cis*-azobenzene back to the *trans* form. By contrast, when a rectangular electric pulse of 5 V ($1\,\mathrm{V\,\mu m^{-1}}$) and 300 ms duration is applied across the solution, recovery of the absorption peak of *trans*-azobenzene indicates fast *cis–trans* isomerization under the low static electric field. The fact that the recovered absorbance is even slightly higher than the initial absorbance suggests the existence of a small amount of *cis*-azobenzene prior to the UV irradiation. Figure 1 b shows the time-resolved increase of the absorbance at 356 nm under a rectangular electric pulse of variable amplitude (0.4–$1\,\mathrm{V\,\mu m^{-1}}$) with a fixed duration of 500 ms. The *cis–trans* isomerization starts at a threshold field of about $0.5\,\mathrm{V\,\mu m^{-1}}$, becomes faster with increasing field strength and can reach completion within 500 ms under 0.8



HHBAzo

---

[*] X. Tong, M. Pelletier, Prof. Dr. A. Lasia, Prof. Dr. Y. Zhao
Département de chimie
Université de Sherbrooke
Sherbrooke, Québec, J1K2R1 (Canada)
Fax: (+1) 819-821-8017
E-mail: yue.zhao@usherbrooke.ca
Homepage: http://pages.usherbrooke.ca/yzhao/

[**] Financial support from the Natural Sciences and Engineering Research Council of Canada and le Fonds québécois de la recherche sur la nature et les technologies of Québec via The Centre for Self-Assembled Chemical Structures (CSACS) is acknowledged. We are grateful to Profs. Patrick Ayotte and Jean Lessard for helpful discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

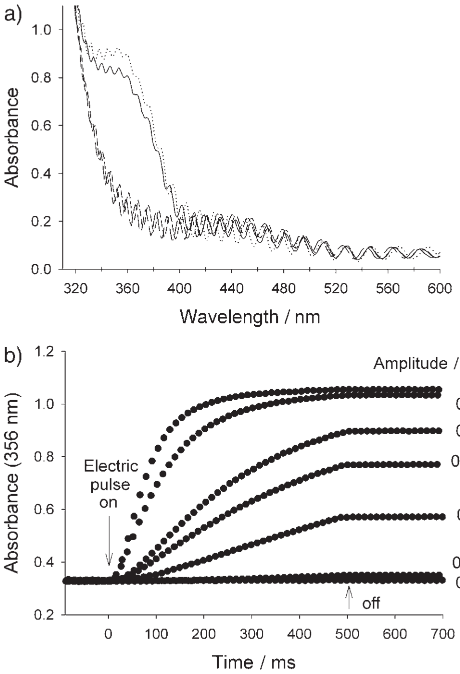


Figure 1. Azobenzene derivative in benzonitrile. a) UV/Vis spectra showing that fast *cis–trans* isomerization occurred under a low static electric field (electric pulse: 1 V μm^{-1}, 300 ms); —— initial solution, – – – immediately after irradiation, ----- 1 h after UV irradiation, ••••• after electric pulses following UV irradiation. b) Kinetics of *cis–trans* isomerization under a 500-ms rectangular electric pulse of various low amplitudes.

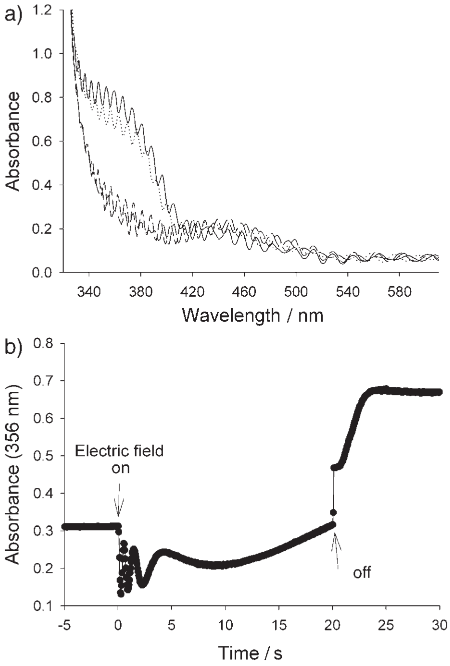


Figure 2. Azobenzene derivative in the nematic liquid crystal 5CB. a) UV/Vis spectra showing the electric-field-induced *cis–trans* isomerization (electric field: 18 V μm^{-1}, 20 s); —— initial mixture, – – – immediately after irradiation, ----- 10 min at 38 °C after UV irradiation, ••••• after electric field following UV irradiation. b) Change in absorbance of the *trans*-azobenzene before, under, and after application of the electric field (electric field: 18 V μm^{-1}, 20 s).

and 1 V μm^{-1}. At $E < 0.8$ V μm^{-1}, *cis–trans* isomerization stops when the voltage is turned off. The electrically induced isomerization appears to be a first-order reaction; fitting the curve at 1 V μm^{-1} yielded a rate constant of about 11.4 s^{-1}, which is six orders of magnitude faster than thermal *cis–trans* isomerization in the absence of the field, which has a rate constant of about 1.15×10^{-5} s^{-1}. We emphasize that the results in Figure 1 b were obtained by using the same solution. That is, after each application of the electric pulse, the solution was re-irradiated with UV light to convert the *trans*-azobenzene back to the *cis*-azobenzene before an electric pulse of a different strength was applied again. The coupled photo- and voltage-induced isomerization processes are reversible. However, isomerization from *trans*- to *cis*-azobenzene under an applied electric field was not observed.

Benzonitrile is a polar solvent having a high dielectric constant ($\varepsilon = 26$ at 20 °C). Even though the benzonitrile used was anhydrous and of high purity (> 99 %), some ions may be present. The question can be raised whether the fast *cis–trans* isomerization may be caused by heating of the solution due to a current flowing through the cell. To answer this question, and to verify the generality of the phenomenon as well, we investigated HHBAzo (ca. 4 %) dissolved in a nematic liquid crystal (LC), namely, 4′-pentyl-4-cyanobiphenyl (5CB, $\varepsilon =$ 14). The results in Figure 2 basically show the same phenomenon for HHBAzo in the LC solvent, although it takes a higher field (18 V μm^{-1}) and longer time (20 s) than in benzonitrile. On UV irradiation *trans–cis* photoisomerization takes place, while after 20 s under the electric field, the *cis*-azobenzene is converted into the *trans* form (Figure 2 a). For the sake of argument, the mixture was purposely heated to 38 °C for 10 min, but the recorded spectrum showed very limited thermal *cis–trans* isomerization of HHBAzo in 5CB (as little as for thermal relaxation 1 h at room temperature after UV irradiation; spectrum not shown). From the result in Figure 2 b, we can deduce that under the applied electric field the mixture could not have a temperature above the nematic–isotropic transition temperature T_{ni} of 5CB (ca. 35 °C). Figure 2 b shows the time-resolved change in absorbance at 356 nm of *trans*-azobenzene in 5CB under the voltage. The apparently peculiar behavior is due to the concomitant change in electric field-induced liquid-crystal orientation. When the voltage is on, the quick drop and oscillating variation in absorbance is caused by the dynamic change in liquid crystal reorientation that alters the transmittance of the mixture, that is, the baseline of the whole spectrum. At longer times (> 8 s), the steady increase in absorbance is due to conversion of the *cis*-azobenzene back to the *trans*-azobenzene. However, *trans*-azobenzene, being liquid-crystalline,[8] is aligned with the surrounding 5CB molecules perpendicular to the substrate surface, so that they cannot absorb the beam of the spectrophotometer. At the end of the electric pulse (field-off), *trans*-azobenzene relaxed with 5CB molecules to lie in the plane, and hence their absorption at 356 nm jumped to the initial level before the UV-induced *trans–cis* photoisomerization. This result indicates that 5CB remains in the nematic phase under the electric field, which is also confirmed by polarizing optical microscopy. Therefore, no heating of the mixture to $T > T_{\mathrm{ni}}$ occurred, because otherwise 5CB would have become an isotropic liquid. This experiment rules out the possibility that the phenomenon comes from thermal relaxation of *cis*-azobenzene due to severe heating of the solution under the electric field.

The fast *cis–trans* isomerization under a low electric field takes place in polar solvents such as benzonitrile and DMSO ($\varepsilon = 48$), as well as in liquid crystals like 5CB and BL006 (a nematic eutectic mixture with a high T_{ni} of 106 °C). However, in nonpolar solvents of decreasing polarity such as dichloroethane ($\varepsilon = 9.1$) and THF ($\varepsilon = 2.4$), *cis–trans* isomerization becomes increasingly difficult. Moreover, the phenomenon is not unique to HHBAzo; it was also observed for a benzonitrile solution of a polymer which contains a different azobenzene derivative, namely, poly{6-[4-(4-cyanophenylazo)phenoxy]hexyl methacrylate ($M \approx 20\,000$; see the Supporting Information).

How can these findings be expained? The electric field applied across the cell containing the azobenzene solution is the external field; the local (i.e., Lorentz field)[9] is actually much higher according to $E_{\mathrm{local}} = (\varepsilon + 2)/3\,E_{\mathrm{external}}$. For HHBAzo dissolved in benzonitrile (Figure 1), the applied $1\ \mathrm{V\,\mu m^{-1}}$ corresponds to a local field of $9.3\ \mathrm{V\,\mu m^{-1}}$, while in 5CB under the applied $18\ \mathrm{V\,\mu m^{-1}}$ (Figure 2), the local field is $96\ \mathrm{V\,\mu m^{-1}}$. However, these local field strengths are still much smaller than the high electric field at the STM junction[6] and within the electric double layer in an electrolyte solution,[4] both of which are in the range of $10^3\ \mathrm{V\,\mu m^{-1}}$. It is thus unlikely that the phenomenon reported here originates from the same mechanism. On the other hand, when an electric field is applied to the azobenzene solution in the ITO-coated cell, it is possible that some existing ions move to the electrodes and develop a higher electric field at the electrode/solution interface, but a high electric field like that associated with the electrical double layer in the electrolyte solution[4] is unlikely. While no experimental evidence indicates that the fast *cis–trans* isomerization is caused by direct interaction of the *cis*-azobenzene with the electric field, a number of experiments support the most probable mechanism responsible for the phenomenon, as described by the following reactions [Eqs. (1)–(3)].[10]

$$\mathrm{R}_{cis} + \mathrm{e}^- \rightarrow \mathrm{R}_{cis}^{-\cdot} \tag{1}$$

$$\mathrm{R}_{cis}^{-\cdot} \rightarrow \mathrm{R}_{trans}^{-\cdot} \tag{2}$$

$$\mathrm{R}_{trans}^{-\cdot} + \mathrm{R}_{cis} \rightarrow \mathrm{R}_{trans} + \mathrm{R}_{cis}^{-\cdot} \tag{3}$$

Indeed, it is known that *cis*-azobenzene in aprotic solvents can be reduced to the radical anion by a one-electron process in an electrochemical cell (in the presence of a supporting electrolyte).[10] In our study, applying an external electric field is equivalent to application of a potential difference between two conductive electrodes. Such a potential difference may cause electrolysis, that is, reduction of *cis*-azobenzene at the cathode and some oxidation reaction on the anode, even in the absence of a supporting electrolyte. The radical anion of *cis*-azobenzene can isomerize to the *trans* radical anion, which in turn can reduce other *cis*-azobenzene in the solution while being oxidized and brought back to the neutral *trans* form.[10] In the ITO-coated LC cell, the azobenzene solution of small volume (due to the small gap of the cell) is in contact with large surfaces of the electrodes, and hence the above reactions could quickly propagate through the bulk solution by diffusion. We also carried out control tests, and the results support the electrochemical origin of the observed phenomenon (see the Supporting Information). We note that although the ITO in the LC cell is coated with a very thin polyimide layer, passage of electric current is allowed.[11]

Although the most probable mechanism is based on the known electrochemical reduction of azobenzene, the reported fast *cis–trans* isomerization of azobenzenes in liquids and liquid crystals without any added supporting electrolytes under a low external electric field was unknown until now. The finding is important because it shows that an electric field can affect the *cis–trans* isomerization of azobenzene derivatives much more easily than previously thought, and this must be taken into account in switching or device applications in which an electric field is involved. In particular, the reversible photoisomerization of azobenzene derivatives has been much used as a photoswitch to alter the optical and electrooptical behavior of LCs;[1] obviously, the conversion of *cis*-azobenzene to the *trans* isomer under an applied electric field may have important consequences for the performance. We designed an experiment to investigate the possible impact of this phenomenon on the properties of azobenzene-doped LCs. Figure 3 a shows the changes in transmittance of nematic BL006 containing 15 % of HHBAzo in response to combined UV exposure and an electric field. In this case, the mixture was filled into a perpendicularly rubbed, ITO-coated LC cell with 5-μm gap, in which LC molecules are aligned to adopt a twist orientation. Between two crossed polarizers, the mixture initially is homogeneous and highly transparent. On UV exposure ($20\ \mathrm{mW\,cm^{-2}}$), the transmittance drops as a result of the phase separation induced by *trans–cis* photoisomerization (a phase rich in *cis*-azobenzene is immiscible with BL006).[8] When the UV light is turned off, the two-phase morphology of the mixture and the reduced transmittance remain quite stable in the dark for several hours due to the very slow thermal *cis–trans* relaxation. In this experiment, however, about 15 s after turning off the UV light, the mixture was subjected to six rectangular electric pulses of 40 V ($8\ \mathrm{V\,\mu m^{-1}}$) and 2-s duration, separated by 20 s of zero voltage. The resulting variation of transmittance reveals the effect of the electric-field-induced *cis–trans* isomerization. With each pulse, when the electric field is on, the transmittance of the mixture drops to the dark state due to the homeotropic orientation of LC molecules (BL006 and HHBAzo) in the two phases, whereas when the field is off the transmittance increases due to orientational relaxation of LC molecules. Interestingly, after the six electric pulses, the transmittance does not recover to the level corresponding to the two-phase morphology formed after UV irradiation inducing *trans-cis* photoisomerization; instead it reaches the initial transmittance of the homogeneous mixture before UV irradiation, which indicates complete conversion of the *cis*-azobenzene back to the *trans* isomer, which is miscible with BL006. The morphological changes giving rise to the observed changes in

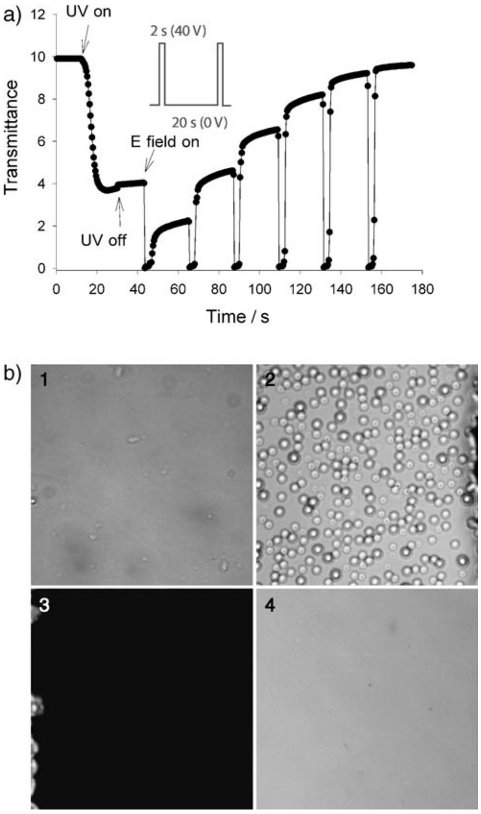


Figure 3. Azobenzene derivative in nematic liquid crystal BL006. a) Changes in transmittance (633-nm probe light) in response to UV irradiation (20 $mW cm^{-1}$) and electric pulses (8 $V \mu m^{-1}$, 2-s duration). b) Polarizing optical micrographs showing the morphological changes of the mixture, which correspond to the changes in transmittance (image area: $50 \times 50\ \mu m^2$): 1) before UV irradiation, 2) after UV irradiation, 3) after switching on the E field, 4) after six electric pulses.

optical transmittance were confirmed by optical microscopy observations under crossed polarizers (Figure 3b).

In conclusion, we have found that a low static electric field can dramatically increase the rate of *cis–trans* isomerization of an azobenzene derivative dissolved in polar liquids and liquid crystals without any added electrolytes. The electrochemical reduction of the *cis*-azobenzene appears to be the origin of the phenomenon. We demonstrated that when azobenzene derivatives are used as photoswitches to change the optical and electrooptical behaviors of liquid crystals, the *cis* isomer may be unstable under an applied voltage due to electric-field-induced *cis–trans* isomerization, which impacts the electrooptical behavior. However, since an electric field can be used to switch the isomeric form of azobenzene derivatives much more easily than previously believed, this finding also opens new opportunities for molecular switches using the combined actions of light and electric fields.

Experimental Section

While HHBAzo was directly dissolved in a given organic solvent (e.g., benzonitrile), to prepare the mixtures with 5CB or BL006, HHBAzo and the liquid crystal were first dissolved in THF, and then THF was removed under reduced pressure. To monitor the electric-field-induced *cis–trans* isomerization by UV/Vis spectroscopy, the sealed ITO-coated cell containing the azobenzene solution was placed in the compartment of a spectrophotometer (Varian 50), and a UV/Vis spot-curing system (Novacure) was used to deliver the UV light for inducing the *trans–cis* photoisomerization in the solution through a flexible light guide fixed in the proximity of the cell. The whole setup was kept in the dark (covered with aluminum foil) during the experiment. A high-voltage waveform generator (WFG500, FLC Electronics) was used to apply electric pulses of various amplitudes and widths across the cell. By using the kinetics software, time-resolved changes in absorbance could be measured with the cell under an electric field following UV irradiation. A picture of the experimental setup, with the different components identified, is given in the Supporting Information.

For the measurements of coupled photooptical and electrooptical behavior, the mixture of HHBAzo with BL006, filled into a cell, was placed between two crossed polarizers, and the transmittance of a probe light (633 nm from a 4-mW He–Ne laser) passing through the cell was measured with a high-speed photodetector (Displaytech) connected to a digital oscilloscope (Tektronix, TDS 420A). Any changes in transmittance of the mixture in response to either UV exposure (photooptical behavior) or an electric pulse (electrooptical behavior) could be monitored to yield information on the photo-induced *trans–cis* photoisomerization or the electric-field-induced *cis–trans* isomerization of HHBAzo. For photoisomerization, UV light was applied to the cell at an angle of about 30° with respect to the cell normal, and by placing a nontransparent plate with a small hole (ca. 2 mm in diameter) in front of the photodetector, the irradiation beam caused no interference in the measured transmittance. The mixture in the cell was equilibrated at 140 °C for 10 min before being cooled to room temperature for the measurement.

Received: December 12, 2007
Revised: February 15, 2008

Keywords: azo compounds · electrooptical properties · isomerization · liquid crystals · photochemistry

[1] a) J. H. Wendorff, M. Eich, B. Reck, H. Ringsdorf, *Macromol. Rapid Commun.* **1987**, *8*, 59; b) Y. Lansac, M. A. Glaser, N. A. Clark, O. D. Lavrentovich, *Nature* **1999**, *398*, 54–57; c) K. Ichimura, *Chem. Rev.* **2000**, *100*, 1847–1873; d) H. Finkelmann, E. Nishikawa, *Phys. Rev. Lett.* **2001**, *87*, 015501; e) A. Natansohn, P. Rochon, *Chem. Rev.* **2002**, *102*, 4139–4175; f) A. Langhoff, F. Giesselmann, *ChemPhysChem* **2002**, *3*, 424–432; g) T. Ikeda, *J. Mater. Chem.* **2003**, *13*, 2037–2057.

[2] C. Barrett, A. Natansohn, P. Rochon, *Macromolecules* **1994**, *27*, 4781–4786.

[3] Z.-F. Liu, K. Hashimoto, A. Fujishima, *Nature* **1990**, *347*, 658–660.

[4] T. Enomoto, H. Hagiwara, D. A. Tryk, Z.-F. Liu, K. Hashimoto, A. Fujishima, *J. Phys. Chem. B* **1997**, *101*, 7422–7427.

[5] J. Henzl, M. Mehlhorn, H. Gawronski, K. H. Rieder, K. Morgenstern, *Angew. Chem.* **2006**, *118*, 617–621; *Angew. Chem. Int. Ed.* **2006**, *45*, 603–606.

[6] M. Alemani, M. V. Peters, S. Hecht, K. H. Rieder, F. Moresco, L. Grill, *J. Am. Chem. Soc.* **2006**, *128*, 14446–14447.

[7] T. Nakabayashi, Md. Wasadoszamen, N. Ohta, *J. Am. Chem. Soc.* **2005**, *127*, 7041–7052.

[8] X. Tong, G. Wang, Y. Zhao, *J. Am. Chem. Soc.* **2006**, *128*, 8746–8747.

[9] C. J. F. Böttcher, *Theory of Electric Polarization*, *Vol. 1*, Elsevier, Amsterdam, **1973**, p. 167.

[10] E. Laviron, Y. Mugnier, *J. Electroanal. Chem.* **1978**, *93*, 69–73.

[11] H.-Y. Chen, K.-X. Yang, W. Lee, *Opt. Express* **2004**, *12*, 3807–3813.